

Mixed Weyl Symbol Calculus and Spectral Line Shape Theory

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Abstract. A new and computationally viable full quantum version of line shape theory is obtained in terms of a mixed Weyl symbol calculus. The basic ingredient in the collision-broadened line shape theory is the time dependent dipole autocorrelation function of the radiator-perturber system. The observed spectral intensity is the Fourier transform of this correlation function. A modified form of the Wigner-Weyl isomorphism between quantum operators and phase space functions (Weyl symbols) is introduced in order to describe the quantum structure of this system. This modification uses a partial Wigner transform in which the radiator-perturber relative motion degrees of freedom are transformed into a phase space dependence, while operators associated with the internal molecular degrees of freedom are kept in their original Hilbert space form. The result of this partial Wigner transform is called a mixed Weyl symbol. The star product, Moyal bracket and asymptotic expansions native to the mixed Weyl symbol calculus are determined. The correlation function is represented as the phase space integral of the product of two mixed symbols: one corresponding to the initial configuration of the system, the other being its time evolving dynamical value. There are, in this approach, two semiclassical expansions — one associated with the perturber scattering process, the other with the mixed symbol star product. These approximations are used in combination to obtain representations of the autocorrelation that are sufficiently simple to allow numerical calculation. The leading $O(\hbar^0)$ approximation recovers the standard classical path approximation for line shapes. The higher order $O(\hbar^1)$ corrections arise from the noncommutative nature of the star product.

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1. Introduction

Collision-broadened spectral line shapes carry important information on the time-dependent dynamical and collisional processes occurring in a radiating medium. For a system consisting of radiators (light emitting or absorbing species) and perturbers (atoms, molecules, ions or electrons), the basic ingredient in spectral line shape theory is the Fourier transform of the time autocorrelation function of the radiator dipole. The physical processes here involve the dynamical evolution of the radiator as it undergoes multiple collisions with a large number of perturbers. The interaction between the time dependent radiator dipole moment and the electromagnetic field induces absorption and emission. In this paper we develop a phase space based representation of quantum mechanics that is suitable for determining this dynamics. Within this formalism there are two different semiclassical approximations. These are employed in tandem to obtain representations of the autocorrelation function that are sufficiently simple to allow numerical calculation.

The method developed here is suggested by the Moyal description[1] of quantum mechanics, which is based on the Wigner–Weyl isomorphism[2] between Hilbert space operators and functions (Weyl symbols) on classical phase space. In this isomorphism[3] the canonical (\hat{q}_i, \hat{p}_i) operators are transformed into linear phase space functions (q_i, p_i) . The line shape problem presents one with two distinguished degrees of freedom: the internal molecular coordinates and the relative radiator–perturber separation variables. In many circumstances (large mass, large impact parameter, high relative velocity, weak pairwise interaction) one expects the relative motion to be nearly classical. On the other hand, evolutions of the subsystems associated with the internal coordinates are, generally, far from classical. This circumstance is exploited by the introduction of a partial Wigner transform that converts the relative motion degrees of freedom into phase space variables, but keeps operators associated with the internal coordinates in their original Hilbert space form. The result of this transformation we call a mixed Weyl symbol.

Our approach to a quantum line shape theory is strongly influenced by the well established ‘classical path approximation’, which is used in many areas of atomic and molecular physics. It assumes that the perturbers move as classical particles, that is, along definite paths determined by the radiator–perturber interaction. The traditional justification for this approximation arises from the notion that one may consider the motion of perturbers in terms of packets of translational wave functions, following the laws of classical mechanics. Anderson[4] in setting up his pioneering line shape theory argued, that since the typical distances of closest approach are about 5\AA , an uncertainty in position of 1\AA leads to no great ambiguity in the magnitude or the type of intermolecular forces involved in the collision. He invoked the uncertainty principle to

conclude that the corresponding uncertainty in velocity is only a few percent for most molecular pairs. The approximation evidently breaks down [5] when the de Broglie wavelength of the perturber is comparable to or larger than a characteristic distance over which the intermolecular potential varies appreciably. An alternative way [6] of expressing this condition is that for the profile to be adequately treated with a classical path, the collisions of significance must have large angular momentum. Such a condition is reminiscent of that required to calculate scattering cross sections classically[7]. Early derivations of the approximation employed heuristic arguments which relied on physical insight. The subsequent work of Baranger[5] and Smith *et al* [8] unified the derivation of the classical path approximation, and in particular employed statistical mechanics to justify the representation of the correlation function as an integral over the phase space variables of the perturber. The phase space average procedure [9] remains a cornerstone of the theory to the present.

The system we shall consider is a dilute gas in which each of the radiator and perturber subsystems is in equilibrium and in which the binary collision approximation is valid. The binary collision approximation, which implies that strong collisions between radiator and perturber are well-separated in time, is a central assumption [10] in most line broadening theories. The radiator density is sufficiently low that the radiator–radiator interaction may be ignored. The linewidth is dominated by collision broadening effects; Doppler and lifetime broadening are omitted from the analysis. The heavy radiator approximation is thereby imposed. The radiator and perturber subsystems are statistically independent; that is, the state of the perturber does not depend explicitly on the state of the radiator and vice versa. This assumption is frequently termed the ‘lack of back reaction’ in the density matrix. Consequently the density matrix may be factored as $\hat{\rho} = \hat{\rho}^{(R)}\hat{\rho}^{(P)}$, where $\hat{\rho}^{(R)}$ and $\hat{\rho}^{(P)}$ depend only on the radiator and perturber variables, respectively [11]. Finally, since interest lies primarily in the effect of the field–radiator interaction on the radiator, the electromagnetic field is treated classically. For an overview of collision–broadening, the reader is referred to the review [6] of Allard and Kielkopf.

A traditional starting point for the development of line shape theory is the expression for the power gained or lost from the radiation field to the molecular many body system in making electric dipole transitions from all initial states i to all possible final states f . The power produced by a single radiator interacting with the perturbers, is given by $\sum_{if} \hbar\omega_{if}\rho_i P_{if}$ where P_{if} is the Fermi Golden Rule probability per unit time for a transition between states i and f having an energy difference $E_i - E_f = \hbar\omega_{if}$. The weight factor ρ_i is the initial state density. The frequency content of this expression is known as the line shape or spectral profile, $I(\omega)$. If $C_N(t)$ is the N -perturber dipole-

dipole autocorrelation function, the spectral profile is the Fourier integral

$$I(\omega) = \frac{1}{\pi} \text{Re} \int_0^\infty dt e^{i\omega t} C_N(t). \quad (1.1)$$

Throughout the paper we employ the version of the binary collision approximation [5, 12], which expresses $C_N(t)$ via the one perturber autocorrelation function $C(t)$, cf. (1.3), namely $C_N(t) = C(t)^N$.

In this setting, the Hamiltonian required in the one perturber autocorrelation function is a sum of three contributions

$$\widehat{H} = \widehat{H}_1 + \widehat{H}_2 + \widehat{H}_{12}. \quad (1.2a)$$

The Hamiltonian \widehat{H}_1 determines the (radiator) molecular structure, and the pair of Hamiltonians $\widehat{H}_2 + \widehat{H}_{12}$ generate different parts of the radiator-perturber dynamics. Let the d_1 dimensional internal radiator coordinates be the Cartesian variables $Q = (Q_1, \dots, Q_{d_1}) \in \mathbf{R}_Q^{d_1}$ and the radiator-perturber coordinates given by $q = (q_1, \dots, q_{d_2}) \in \mathbf{R}_q^{d_2}$. The state spaces over these two independent coordinate manifolds are $\mathcal{H}_1 = L^2(\mathbf{R}^{d_1})$ and $\mathcal{H}_2 = L^2(\mathbf{R}^{d_2})$. The full system Hilbert space is $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2 = L^2(\mathbf{R}^{d_1} \times \mathbf{R}^{d_2})$. For reasons of clarity of presentation and notational convenience, we assume that the perturber may be treated as a point particle. This means that q is a three dimensional vector ($d_2 = 3$). The mixed Weyl symbol calculus and line shape theory developed here are valid for all values of d_1 and d_2 . If desired, the one perturber Hamiltonian (1.2a) may be extended to a many perturber system.

The Hamiltonians \widehat{H}_1 and \widehat{H}_2 are simple in the sense that they are tensor products of operators on \mathcal{H}_1 and \mathcal{H}_2 , namely $\widehat{H}_1 = \widehat{h}_1 \otimes I_2$ and $\widehat{H}_2 = I_1 \otimes \widehat{h}_2$, where I_i is the identity on \mathcal{H}_i . The Hamiltonian \widehat{h}_1 and its associated eigenvalue problem $\widehat{h}_1|\Phi_n\rangle = E_n|\Phi_n\rangle$ determine the energy spectrum and wave functions of the radiator. The wave function $|\Phi_1\rangle$ is the molecular groundstate. If $\widehat{h}_{2,0}$ is the perturber kinetic energy and \widehat{v}_2 is a Q -independent (isotropic) part of the intermolecular interaction energy, then $\widehat{h}_2 \equiv \widehat{h}_{2,0} + \widehat{v}_2$. The operator \widehat{H}_{12} includes all the anisotropic parts of the radiator-perturber potential. It depends on the relative orientation of the molecular axis and the vector q . This operator is a function of both q and Q . For example in the case where the radiator can be treated as a rigid rotor ($d_1 = 3$), then \widehat{H}_{12} has the Legendre polynomial expansion

$$\widehat{H}_{12} = \sum_{l=0}^{\infty} V_{12}^{(l)}(|q|) P_l(\widehat{q} \cdot \widehat{Q}). \quad (1.2b)$$

The multipole potentials $V_{12}^{(l)}(|q|)$ are phenomenologically known functions. The presence of the $V_{12}^{(0)}$ term in (1.2b) allows one to include portions of the isotropic potential in \widehat{H}_{12} .

The dipole autocorrelation function [4, 5, 12] generated by the dynamics of \widehat{H} is

$$C(t) = \text{Tr}_{\mathcal{H}} \left(\widehat{\mu}_j U(H; t)^\dagger \widehat{\mu}_j U(H; t) \widehat{\rho} \right). \quad (1.3)$$

In the formula above, $U(H; t) \equiv \exp(-i\widehat{H}t/\hbar)$ denotes Schrödinger picture evolution and $\widehat{\mu}_j$ is the j th Cartesian component of the radiator electric dipole. Tensors with repeated indices such as $j \in (1, 2, 3)$ are summed over. The initial ($t = 0$) thermal state of the system is specified by the density matrix $\widehat{\rho} = e^{-\beta\widehat{H}}/\text{Tre}^{-\beta\widehat{H}}$, where $\beta = (kT)^{-1}$. The statistical structure of the radiator–perturber system is normally assumed to be a stationary ergodic ensemble with temperature T . In this case the canonical ensemble average on the right-hand side of (1.3) is equivalent to the long time average over many radiator–perturber collisions. An attractive feature of the correlation function $C(t)$ is that the effects of statistics (via $\widehat{\rho}$) and dynamics (via $U(H; t)$) are clearly separated.

Our approach to computing $C(t)$ is to generalize the existing Moyal quantum mechanics so that it can predict the \widehat{H} dynamics in the full Hilbert space \mathcal{H} . In order to see the possible relevance of the Wigner transform methods to the classical path approximation, consider in isolation the one body (perturber) problem generated by \widehat{h}_2 on $\mathcal{H}_2 = L^2(\mathbf{R}^{d_2})$. Adapted to this setting, the key elements [3] of the Moyal theory are as follows. Operators \widehat{A} on \mathcal{H}_2 may be represented as functions (Weyl symbols) on phase space. The relevant phase space, with variables $z = (q, p)$, is that induced by the manifold $\mathbf{R}_q^{d_2}$, namely $T_2^* \equiv T^*(\mathbf{R}_q^{d_2}) \simeq \mathbf{R}_q^{d_2} \times \mathbf{R}_p^{d_2}$. We label the Wigner transform[13] map σ , i.e. $\sigma\widehat{A}(z) = A_w(z)$, where

$$A_w(z) = \int_{\mathbf{R}^{d_2}} dx e^{-ip \cdot x/\hbar} \langle q + \tfrac{1}{2}x | \widehat{A} | q - \tfrac{1}{2}x \rangle. \quad (1.4)$$

The Fourier transform nature of the Wigner correspondence (1.4) ensures that it has an inverse, σ^{-1} .

The Heisenberg picture evolution generated by \widehat{h}_2 has two equivalent realizations. In Hilbert space \mathcal{H}_2 , one has $\widehat{A}(t) \equiv \mathbf{\Gamma}(h_2; t)\widehat{A} = U(h_2, t)^\dagger \widehat{A} U(h_2; t)$. In symbol space the equivalent of $\mathbf{\Gamma}(h_2; t)$ is denoted by $\Gamma(h_2; t) \equiv \sigma\mathbf{\Gamma}(h_2; t)\sigma^{-1}$. This latter operator maps symbols to symbols. In detail, if $A_w(z)$ is the Weyl symbol of \widehat{A} at $t = 0$ and $A(t|z) \equiv (\widehat{A}(t))_w(z)$ is the corresponding dynamical value at time t , then

$$\Gamma(h_2; t) A_w(z) = A(t|z). \quad (1.5a)$$

Acting on suitable symbols, $\Gamma(h_2; t)$ defines a one parameter group with the same structure one finds with $\mathbf{\Gamma}(h_2; t)$, namely, $\Gamma(h_2; t_1 + t_2) = \Gamma(h_2; t_2)\Gamma(h_2; t_1)$. The equation of motion for $A(t|z)$ follows from taking the Wigner transform of the Heisenberg equation for $\widehat{A}(t)$,

$$\frac{\partial}{\partial t} A(t|z) = \{A(t), h_2\}_M(z). \quad (1.5b)$$

Here $\{\cdot, \cdot\}_M$ is the Moyal bracket, cf. (2.11b), of the symbol pair $A(t)$ and $h_2 \equiv (\widehat{h}_2)_w$.

Given the solution of (1.5b), expectation values in \mathcal{H}_2 are realized as integrals over T_2^* . Let $\psi \in \mathcal{H}_2$ be a unit normalized initial state defining a density matrix $\widehat{\rho} = |\psi\rangle\langle\psi|$.

In terms of the Wigner distribution $w_\psi(z) = (h)^{-d_2}(\hat{\rho})_w(z)$, ($h = 2\pi\hbar$);

$$\langle \hat{A}(t) \rangle_\psi = \text{Tr}_{\mathcal{H}_2} \hat{\rho} \hat{A}(t) = \int_{T_2^*} dz w_\psi(z) \Gamma(h_2; t) A_w(z). \quad (1.6a)$$

In the circumstances where h_2 is \hbar -independent, $\Gamma(h_2; t)$ admits a small \hbar asymptotic expansion

$$\Gamma(h_2; t) A_w = \sum_{n=0}^{\infty} \frac{\hbar^{2n}}{(2n)!} \gamma^{(2n)}(h_2; t) A_w = \left[\gamma^{(0)}(h_2; t) + \frac{\hbar^2}{2!} \gamma^{(2)}(h_2; t) \right] A_w + O(\hbar^4). \quad (1.6b)$$

Like $\Gamma(h_2; t)$, the quantities $\gamma^{(2n)}(h_2; t)$ are maps on symbols. In reference [3] explicit formulas for $\gamma^{(2n)}(h_2; t)$ were derived as a result of a connected graph representation for $\Gamma(h_2; t)$. The leading term $\gamma^{(0)}(h_2; t)$ (as has long been known [14, 15, 16]) is determined by the h_2 generated classical flow. The higher order operator coefficients, beginning with $\gamma^{(2)}(h_2; t)$, have the form of partial differential operators [cf. (3.7c)] acting on symbols. Combining expansion (1.6b) and (1.6a) yields a semiclassical expansion for the expectation value $\langle \hat{A}(t) \rangle_\psi$. With suitable restrictions on A_w , rigorous error bound estimates are available for the asymptotic expansion (1.6b). The early work of Antonets [14] verified, for finite time displacements $t \in [0, T]$, that $\Gamma(h_2, t) A_w \rightarrow \gamma^{(0)}(h_2; t) A_w$ in an appropriate norm as $\hbar \rightarrow 0$. More recently new proofs [17] have been constructed that obtain error estimates that hold for arbitrary time displacements.

The principal goal of this paper is to derive a modified version of Moyal quantum mechanics that treats the perturber degrees of freedom with a phase space formalism like (1.5)–(1.6) while maintaining a consistent \mathcal{H}_1 -operator valued description of the radiator degrees of freedom. Within this hybrid operator–symbol formalism, the Moyal bracket induces a natural semiclassical expansion. The leading approximation is shown to recover the classical path approximation. Higher order corrections are well defined and sufficiently simple to allow numerical calculation.

2. Mixed Weyl Symbol Calculus

The *mixed Weyl symbol* is a parametric family of operators that arises when a phase space function is quantized in a subset of its canonical variables. The conventional symbol is a complex valued function in phase space, whereas the mixed Weyl symbol is operator valued. In this section, we modify the Wigner transform[13] and Weyl quantization[18] procedures so that they define a mixed Weyl symbol formalism. Within this formalism we construct representations of the noncommutative star product, the Moyal bracket[1] and the trace formulas that determine expectation values. The asymptotic expansions, which form the basis of a semiclassical analysis, are also obtained.

Each of the \mathcal{H}_i subspace components of $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$ has its own set of canonical operators and coordinates. We distinguish these variables by employing upper case

letters for \mathcal{H}_1 and lower case for \mathcal{H}_2 . The d_1 system classical phase space is $T_1^* \equiv T^*(\mathbf{R}_Q^{d_1}) \simeq \mathbf{R}_Q^{d_1} \times \mathbf{R}_P^{d_1}$ with coordinates $Z = (Z_1, \dots, Z_{2d_1}) = (Q_1, \dots, Q_{d_1}; P_1, \dots, P_{d_1})$. In the Hilbert space \mathcal{H}_1 over \mathbf{R}^{d_1} , the quantized coordinate operators are $\hat{Z} = (\hat{Q}, \hat{P}) = (\hat{Q}_1, \dots, \hat{Q}_{d_1}; \hat{P}_1, \dots, \hat{P}_{d_1})$. Acting on $\mathbf{R}_Q^{d_1}$ space wave functions $\Phi \in \mathcal{H}_1$, the \hat{Q}_j are the operators of multiplication by Q_j and the conjugate momentum are $\hat{P}_j = -i\hbar\partial/\partial Q_j$. Likewise the d_2 system has phase space $T_2^* \equiv T^*(\mathbf{R}_q^{d_2})$ with variables $z = (q_1, \dots, q_{d_2}; p_1, \dots, p_{d_2})$ and canonical operators $\hat{z} = (\hat{q}_1, \dots, \hat{q}_{d_2}; \hat{p}_1, \dots, \hat{p}_{d_2})$.

The commutation relations

$$[\hat{Z}_\alpha, \hat{Z}_\beta] = i\hbar J_{\alpha\beta}^{(1)}, \quad [\hat{z}_\mu, \hat{z}_\nu] = i\hbar J_{\mu\nu}^{(2)}, \quad [\hat{Z}_\alpha, \hat{z}_\mu] = 0, \quad (2.1a)$$

state the separate canonical character and mutual independence of \hat{Z} and \hat{z} . The matrices $J^{(1)}$ and $J^{(2)}$ are the standard symplectic matrices that arise on T_1^* and T_2^* . In block form

$$J^{(1)} = \begin{bmatrix} 0 & \delta^{d_1} \\ -\delta^{d_1} & 0 \end{bmatrix}, \quad J^{(2)} = \begin{bmatrix} 0 & \delta^{d_2} \\ -\delta^{d_2} & 0 \end{bmatrix}, \quad (2.1b)$$

where δ^{d_i} are the d_i -dimensional identity matrices. The transformations J are invertible with $J^{-1} = J^T = -J$.

2.1. Partial Quantization

In order to help formulate a statement of partial quantization, we recall the definition of the Weyl symbol appropriate for the full phase space $T_{1+2}^* \equiv T^*(\mathbf{R}_Q^{d_1} \times \mathbf{R}_q^{d_2}) \simeq T_1^* \times T_2^*$. All the phase spaces T_1^*, T_2^* and T_{1+2}^* are Euclidean. In this circumstance, the conventional Wigner transform [13, 19, 2] is well defined. It maps an operator \hat{A} on \mathcal{H} into a complex valued function that is supported on T_{1+2}^* . Specifically, if $\langle X, x | \hat{A} | X', x' \rangle$ denotes the coordinate space Dirac kernel of \hat{A} , then the Weyl symbol is

$$A_w(Z; z) \equiv \iint dX dx e^{-i(P \cdot X + p \cdot x)/\hbar} \langle Q + \tfrac{1}{2}X, q + \tfrac{1}{2}x | \hat{A} | Q - \tfrac{1}{2}X, q - \tfrac{1}{2}x \rangle. \quad (2.2a)$$

Formula (2.2a) is a restatement of (1.4) adjusted to the larger phase space T_{1+2}^* . This (full) Wigner transform mapping $\hat{A} \mapsto A_w$ is always denoted by σ , independent of which Hilbert space $\mathcal{H}, \mathcal{H}_1$ or \mathcal{H}_2 that \hat{A} acts on, i.e. $A_w = \sigma \hat{A}$.

The invertibility of the Fourier transform in (2.2a) means that σ has an inverse σ^{-1} . The map $\sigma^{-1}A_w = \hat{A}$ is Weyl quantization. The action of σ^{-1} on exponential functions is $\sigma^{-1}[\exp(iU \cdot Z + iu \cdot z)] = \exp(iU \cdot \hat{Z} + iu \cdot \hat{z})$, and may be viewed as the basis of Weyl quantization. Superposition of this result provides the quantization for arbitrary phase space functions. Suppose a is the Fourier transform of $A_w : T_{1+2}^* \rightarrow \mathbf{C}$, then

$$A_w(Z; z) = \iint dU du a(U; u) e^{i(U \cdot Z + u \cdot z)}, \quad (2.2b)$$

$$\hat{A} = \iint dU du a(U; u) e^{i(U \cdot \hat{Z} + u \cdot \hat{z})}. \quad (2.2c)$$

To verify that Weyl quantization (2.2c) is the inverse of the Wigner transform (2.2a), it suffices to take the $|X, x\rangle$ Dirac matrix elements of (2.2c). Fourier transform identities lead one to recover the Wigner transform (2.2a).

It is evident from the structure of (2.2c) and the independence of the operators \hat{Z}, \hat{z} that one may partially quantize A_w . In this context the two relevant choices are

$$\hat{A}_{w1}(Z) = (\tilde{\sigma}_2^{-1} A_w)(Z) \equiv \iint dU du a(U; u) e^{iU \cdot Z} e^{iu \cdot \hat{z}}, \quad (2.3a)$$

$$\hat{A}_{w2}(z) = (\tilde{\sigma}_1^{-1} A_w)(z) \equiv \iint dU du a(U; u) e^{iU \cdot \hat{Z}} e^{iu \cdot z}. \quad (2.3b)$$

In the notation above, the maps $\tilde{\sigma}_2^{-1}$ and $\tilde{\sigma}_1^{-1}$ are the partial Weyl quantizations of A_w with respect to the z and Z variables. The object $\hat{A}_{w1}(Z)$ is an operator family on \mathcal{H}_2 with a parametric dependence on Z . Likewise, $\hat{A}_{w2}(z)$ is an operator on \mathcal{H}_1 .

The subscript labeling w1 and w2 used in (2.3) is suggested by the Wigner transform point of view. For example, the w1 subscript on $\hat{A}_{w1}(Z)$ reminds one that the first argument of \hat{A} , namely \hat{Z} , has been dequantized to become a parametric dependence on Z .

To pass from \hat{A}_{w1} or \hat{A}_{w2} to \hat{A} , one Weyl quantizes, respectively, either $e^{iU \cdot Z}$ or $e^{iu \cdot z}$ in (2.1). After a Fourier transform this gives

$$\hat{A} = \sigma_1^{-1} \hat{A}_{w1} \equiv \frac{1}{(2\pi)^{2d_1}} \iint dU dZ \hat{A}_{w1}(Z) e^{iU \cdot (\hat{Z} - Z)}, \quad (2.4a)$$

$$\hat{A} = \sigma_2^{-1} \hat{A}_{w2} \equiv \frac{1}{(2\pi)^{2d_2}} \iint du dz \hat{A}_{w2}(z) e^{iu \cdot (\hat{z} - z)}. \quad (2.4b)$$

One may implement the transform $A_w \mapsto \hat{A}$ via the a or b combinations of (2.3) and (2.4). This freedom to choose the order of the partial quantizations is a consequence of the mutual commutivity of \hat{Z} and \hat{z} . The product mappings that characterize these two equivalent quantization orderings are

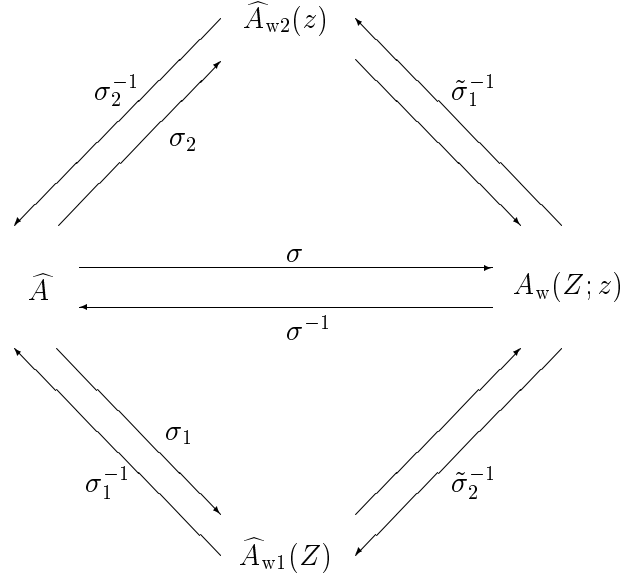
$$\hat{A} = \sigma^{-1} A_w = \sigma_1^{-1} \tilde{\sigma}_2^{-1} A_w = \sigma_2^{-1} \tilde{\sigma}_1^{-1} A_w. \quad (2.5a)$$

To complete the list of transformations we require the partial Wigner transforms $\sigma_1 \hat{A} = \hat{A}_{w1}$ and $\sigma_2 \hat{A} = \hat{A}_{w2}$. In view of (2.2a), (2.3) we have the definitions

$$\sigma_1 \hat{A} \equiv \tilde{\sigma}_2^{-1} \sigma \hat{A}, \quad \sigma_2 \hat{A} \equiv \tilde{\sigma}_1^{-1} \sigma \hat{A}. \quad (2.5b)$$

It is straightforward to verify that σ_j^{-1} and σ_j ($j = 1, 2$) are mutual inverses. The reason we have elected to define σ_1 and σ_2 by the product of transformations in (2.5b) rather than by the direct route from \hat{A} to \hat{A}_{w1} or \hat{A}_{w2} via an integral like (2.2a) is that the latter requires a non-standard form of the Dirac ket. Namely, instead of matrix elements of \hat{A} with respect to the full ket $|X, x\rangle$ one would need matrix elements in terms of a partial ket $|x\rangle$.

The identification and interdependence of the various mixed symbols and partial quantizations are displayed in Fig. 1.

**Figure 1.** Mixed Symbol Mappings

It is instructive to contrast the basic features of the full Wigner–Weyl isomorphism σ with those induced by the partial transformations σ_i . Consider the tensor product operator $\hat{A} = \hat{f} \otimes \hat{g}$ on $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$. The σ_2 transform of \hat{A} has the factored form $\sigma_2(\hat{f} \otimes \hat{g})(z) = g(z)\hat{f}$, where $g(z) = (\sigma\hat{g})(z)$, cf. (1.3). In this example the z parametric dependence resides in the \mathbf{C} -valued multiplier $g(z)$. This means that the resultant families of operators commute, e.g. $[g(z)\hat{f}, g(z')\hat{f}] = 0$ for all z, z' . However, for a general operator \hat{A} , the different operators in the family $\hat{A}_{w2}(z)$ will not commute.

A similar example concerns the σ_2 image of $\hat{f} \otimes \hat{z}_\alpha$. Let π_α be the linear coordinate functions on T_2^* , i.e. $\pi_\alpha(z) = z_\alpha$. The σ_2 Wigner transform maps this operator into

$$\sigma_2(\hat{f} \otimes \hat{z}_\alpha)(z) = (\sigma\hat{z}_\alpha)(z)\hat{f} = \pi_\alpha(z)\hat{f}. \quad (2.6)$$

All the transformations $\sigma, \sigma_1, \sigma_2$ are linear bijective correspondences. A simplifying aspect of these transformations is the reality feature. Selfadjoint operators $\hat{A} = \hat{A}^\dagger$ have real valued Weyl symbols $A_w(Z; z) = A_w(Z; z)^*$, and Hermitian valued mixed symbols $\hat{A}_{w2}(z) = \hat{A}_{w2}(z)^\dagger$.

2.2. Symbol Products and the Moyal Bracket

The $*$ product of symbols [2, 20, 21] is constructed so that the noncommutative product structure of operators on Hilbert space is accurately mirrored in the space of symbols. For operators \hat{X}, \hat{Y} on \mathcal{H} with symbols X_w, Y_w the conventional $*$ product is $X_w * Y_w \equiv \sigma(\hat{X}\hat{Y})$. By definition, this product is noncommutative. The mixed symbol

'star' is obtained via the same procedure. In terms of \widehat{X}_{w2} and \widehat{Y}_{w2} , let

$$\widehat{X}_{w2} * \widehat{Y}_{w2} \equiv \sigma_2(\widehat{X}\widehat{Y}) . \quad (2.7a)$$

Of course, there is a different 'star' product for each of the symbols A_w , \widehat{A}_{w1} and \widehat{A}_{w2} . We denote all of these products by the same character $*$. The values of the surrounding symbols will determine the selection of the relevant 'star' operation.

A basic representation of the σ_2 -star product is given by the integral formula[22]

$$\widehat{X}_{w2} * \widehat{Y}_{w2}(z) = \left(\frac{\lambda}{\pi}\right)^{2d_2} \iint dz' dz'' \widehat{X}_{w2}(z+z') \widehat{Y}_{w2}(z+z'') \exp \left[2i\lambda(z' \cdot J^{(2)} z'') \right] , \quad (2.7b)$$

where $\lambda = \hbar^{-1}$. Whenever the integral exists, it provides an exact formula for $\widehat{X}_{w2} * \widehat{Y}_{w2}$. A distinguishing feature here is that the integrand is a product of two noncommuting \mathcal{H}_1 valued operators. This formula is verified by expressing $\widehat{X}\widehat{Y}$ in terms of two copies of (2.4b) and using the Baker–Cambell–Hausdorff identity $\exp(iu' \cdot \widehat{z}) \exp(iu'' \cdot \widehat{z}) = \exp(-i\frac{\hbar}{2}u' \cdot J^{(2)}u'') \exp(i(u' + u'') \cdot \widehat{z})$. Acting with σ_2 on the $\widehat{X}\widehat{Y}$ product, while employing $\sigma_2 \exp(i(u' + u'') \cdot \widehat{z}) = \exp(i(u' + u'') \cdot z)$, leads to (2.7b). Formula (2.7b) also represents the σ -star product if the quantities $\widehat{X}_{w2}, \widehat{Y}_{w2}$ are replaced with \mathbf{C} -valued symbols.

The mixed symbol Moyal bracket is the σ_2 image of the commutator $[\widehat{X}, \widehat{Y}]$, specifically

$$i\hbar\{\widehat{X}_{w2}, \widehat{Y}_{w2}\}_M \equiv \widehat{X}_{w2} * \widehat{Y}_{w2} - \widehat{Y}_{w2} * \widehat{X}_{w2} = \sigma_2[\widehat{X}, \widehat{Y}] . \quad (2.7c)$$

As with the $*$ notation, the appropriate meaning of the bracket $\{\cdot, \cdot\}_M$ is selected by the values of its argument symbols. In all cases, the Moyal bracket is bilinear, skew and obeys the Jacobi identity. The Lie algebra defined by the Moyal bracket is isomorphic to the Lie algebra induced by the commutator of operators on \mathcal{H} .

2.3. Star Product Asymptotics

In many circumstances the $*$ product is close to commutative multiplication, and the difference of these two products is described by an asymptotic expansion involving derivatives of symbols. In this subsection we construct derivative expansions for mixed Weyl symbols and summarize their asymptotic structure.

Asymptotic expansions of the $*$ product are a consequence of the large λ limit of the integral (2.7b). In these expansions it is desirable to have an effective small \hbar scaling, but our line shape application requires that Planck's constant be fixed at its physical value, $\hbar = 1.055 \times 10^{-34}$ J.s. In order to accommodate these opposing demands, we set $\lambda = (\epsilon\hbar)^{-1}$ in (2.7b), and effect the small \hbar scaling by letting the dimensionless parameter $\epsilon \rightarrow 0$.

First recall Groenewold's [23, 24] expansion for \mathbf{C} -valued symbols. Suppose the

operators \hat{f}, \hat{g} on \mathcal{H}_2 have symbols $f = \sigma(\hat{f}), g = \sigma(\hat{g})$. For small ϵ , one has

$$f * g(z) = \sum_{n=0}^{N-1} \frac{1}{n!} \left(\frac{i\epsilon\hbar}{2} \right)^n J_{\mu_1\nu_1}^{(2)} \cdots J_{\mu_n\nu_n}^{(2)} f_{;\mu_1\cdots\mu_n}(z) g_{;\nu_1\cdots\nu_n}(z) + R_N(z) \quad (2.8a)$$

$$= f(z)g(z) + \frac{i\epsilon\hbar}{2} \{f, g\}(z) + O(\epsilon^2). \quad (2.8b)$$

The first term on the right of (2.8b) is ordinary multiplication, while the term linear in ϵ is the Poisson bracket, $\{f, g\} = \nabla f \cdot J^{(2)} \nabla g$. The tensor indices $\mu_1 \cdots \mu_n$ on f and g denote the partial derivative $\partial^n / \partial z_{\mu_1} \cdots \partial z_{\mu_n}$. The remainder $R_N(z)$ is $O(\epsilon^N)$.

We require expansions analogous to (2.8) in which f and g are replaced by mixed Weyl symbols. A useful derivative notation adapted to the Groenewold type expansion is the following. Denote by B the extended Poisson bracket operator for T_2^* . The B operator acts on a tuple of mixed Weyl symbols $\prec \widehat{X}_{w2}, \widehat{Y}_{w2} \succ$ to produce a new mixed Weyl symbol. The first and higher iterates of B are

$$B \prec \widehat{X}_{w2}, \widehat{Y}_{w2} \succ(z) \equiv J_{\mu\nu}^{(2)} \widehat{X}_{w2;\mu}(z) \widehat{Y}_{w2;\nu}(z), \quad (2.9a)$$

$$B^n \prec \widehat{X}_{w2}, \widehat{Y}_{w2} \succ(z) \equiv J_{\mu_1\nu_1}^{(2)} \cdots J_{\mu_n\nu_n}^{(2)} \widehat{X}_{w2;\mu_1\cdots\mu_n}(z) \widehat{Y}_{w2;\nu_1\cdots\nu_n}(z) \quad (2.9b)$$

$$= (-1)^n J_{\nu_1\mu_1}^{(2)} \cdots J_{\nu_n\mu_n}^{(2)} \widehat{X}_{w2;\mu_1\cdots\mu_n}(z) \widehat{Y}_{w2;\nu_1\cdots\nu_n}(z). \quad (2.9c)$$

The equivalent pair of representations (2.9b) and (2.9c) for B^n follow from the skew nature of $J^{(2)}$, namely $J_{\mu\nu}^{(2)} = -J_{\nu\mu}^{(2)}$. Clearly $B \prec \widehat{X}_{w2}, \widehat{Y}_{w2} \succ(z)$ has the derivative structure of a Poisson bracket on T_2^* , but with operator valued rather than scalar valued arguments. The quantity $\hbar B$ is dimensionless.

The generalization of the Groenewold expansion to the mixed symbol $*$ product is

$$\widehat{X}_{w2} * \widehat{Y}_{w2}(z) = \exp(i\epsilon\hbar B/2) \prec \widehat{X}_{w2}, \widehat{Y}_{w2} \succ(z) \quad (2.10a)$$

$$= \widehat{X}_{w2}(z) \widehat{Y}_{w2}(z) + \frac{i\epsilon\hbar}{2} B \prec \widehat{X}_{w2}, \widehat{Y}_{w2} \succ(z) + \cdots. \quad (2.10b)$$

Formula (2.10) indicates how the $*$ operator modifies the \mathcal{H}_1 product of two mixed symbols, $\widehat{X}_{w2}(z)$ and $\widehat{Y}_{w2}(z)$. Clearly, in the algebra of mixed symbols, $\widehat{X}_{w2}(z)$, one has two noncommutative mechanisms — the $*$ operation and the noncommutative \mathcal{H}_1 operator product.

As $\lambda \rightarrow \infty$ the exponential in (2.7b) oscillates rapidly. This circumstance justifies an application of the stationary phase method [25] and leads to the asymptotic expansion (2.10b). In order to establish the equivalent formal identity (2.10a), express the $\widehat{X}\widehat{Y}$ product as a multiple integral by using representation (2.4b). In the integrand one encounters $\exp(-\frac{i\hbar}{2} u \cdot J^{(2)} u') \exp(i(u + u') \cdot z)$. Rewrite this as $\exp(\frac{i\hbar}{2} \nabla_z \cdot J^{(2)} \nabla_{z'}) \exp(iu \cdot z + iu' \cdot z')|_{z=z'}$ and take the left exponential operator outside the $du du'$ integration. This gives (2.10a).

An important application of (2.10) arises when the expansion is used to describe the σ_2 -Moyal bracket. Using the equivalence of (2.9b) and (2.9c) the exponential series

reorganizes as

$$\begin{aligned} i\hbar\{\widehat{X}_{w2}, \widehat{Y}_{w2}\}_M(z) &= \cos\left(\frac{\epsilon\hbar}{2}B\right) \prec \widehat{X}_{w2}, \widehat{Y}_{w2} \succ_- (z) \\ &\quad + i \sin\left(\frac{\epsilon\hbar}{2}B\right) \prec \widehat{X}_{w2}, \widehat{Y}_{w2} \succ_+ (z) \end{aligned} \quad (2.11a)$$

$$= [\widehat{X}_{w2}(z), \widehat{Y}_{w2}(z)] + \frac{i\epsilon\hbar}{2}B \prec \widehat{X}_{w2}, \widehat{Y}_{w2} \succ_+ (z) + O(\epsilon^2). \quad (2.11b)$$

Here $\prec \widehat{X}_{w2}, \widehat{Y}_{w2} \succ_{\pm} = \prec \widehat{X}_{w2}, \widehat{Y}_{w2} \succ \pm \prec \widehat{Y}_{w2}, \widehat{X}_{w2} \succ$ denotes the symmetrized and anti-symmetrized tuple, respectively. Whenever the operator families $\widehat{X}_{w2}(z)$ and $\widehat{Y}_{w2}(z')$ commute, the cosine contribution vanishes and one recovers the familiar [1] sine function version of the Moyal bracket.

The parameter $\epsilon \in [0, 1]$ measures the deformation of the $*$ product from the conventional $\epsilon = 0$ product. It provides a one dimensional variable that allows one to characterize the derivative expansions, (2.8) and (2.10), as $\epsilon \rightarrow 0$ asymptotic approximations of the $*$ operation. However, even if $\epsilon = 1$ and there is no exposed small parameter, the Groenewold formulas (2.8) and (2.10) may still be valid asymptotic expansions. (See Appendix A).

2.4. Trace Identities

Quantum expectation values are determined, within the density matrix formalism, by traces of operators on \mathcal{H} . For the σ -transform the quantum trace is realized by a phase space integral. Assuming that \widehat{Y} and $\widehat{Y}\widehat{X}$ are trace class on \mathcal{H} with smooth symbols, the known [26, Chap. IV] trace representations are

$$\text{Tr}_{\mathcal{H}} \widehat{Y} = \frac{1}{h^{d_1+d_2}} \iint_{T_{1+2}^*} dZ \, dz \, Y_w(Z, z), \quad (2.12a)$$

$$\text{Tr}_{\mathcal{H}} \widehat{Y}\widehat{X} = \frac{1}{h^{d_1+d_2}} \iint_{T_{1+2}^*} dZ \, dz \, Y_w(Z, z) X_w(Z, z). \quad (2.12b)$$

Our study of dynamics will systematically employ the mixed symbols $\widehat{Y}_{w2}(z)$ and $\widehat{X}_{w2}(z)$, thus we require the σ_2 -counterparts of (2.4). One finds

$$\text{Tr}_{\mathcal{H}} \widehat{Y} = \frac{1}{h^{d_2}} \int_{T_2^*} dz \, \text{Tr}_{\mathcal{H}_1} \widehat{Y}_{w2}(z), \quad (2.13a)$$

$$\text{Tr}_{\mathcal{H}} \widehat{Y}\widehat{X} = \frac{1}{h^{d_2}} \int_{T_2^*} dz \, \text{Tr}_{\mathcal{H}_1} \widehat{Y}_{w2}(z) * \widehat{X}_{w2}(z). \quad (2.13b)$$

The proofs of (2.13) are simple. To show (2.13a), write the trace on \mathcal{H}_1 in terms of the Dirac integral kernel, viz. $\text{Tr}_{\mathcal{H}_1} \widehat{Y}_{w2}(z) = \int dX \, \langle X | \widehat{Y}_{w2}(z) | X \rangle$. Now express $\widehat{Y}_{w2}(z)$ via (2.3b) and use the fact that $\langle X | \exp(iU_1 \cdot \widehat{Q} + iU_2 \cdot \widehat{P}) | X \rangle = \exp(iU_1 \cdot X) \delta^{d_1}(\hbar U_2)$. If one computes the right hand side of (2.13a) the various Fourier integrals all become

delta functions, giving a result that is the $dZ dz$ integral on the right of (2.12a). This establishes (2.13a).

Formula (2.13b) is a consequence of (2.13a), if \widehat{X} is replaced by $\widehat{Y}\widehat{X}$ in (2.13a). A further simplification of (2.13b) allows one to replace the integrand by $\text{Tr}_{\mathcal{H}_1} \widehat{Y}_{w2}(z) \widehat{X}_{w2}(z)$. In order to see this notice that an integration by parts shows

$$\int dz J_{\mu\nu}^{(2)} \widehat{X}_{w2;\mu}(z) \widehat{Y}_{w2;\nu}(z) = - \int dz J_{\mu\nu}^{(2)} \widehat{X}_{w2}(z) \widehat{Y}_{w2;\mu\nu}(z) = 0 . \quad (2.14)$$

In the rightmost integral, the skew matrix $J_{\mu\nu}^{(2)}$ times the $\mu\nu$ symmetric operator $\widehat{Y}_{w2;\mu\nu}(z)$ sums to zero. A similar argument shows that the higher order B^n terms vanish.

The mathematical analysis of this section is heuristic and formal in style. Our intention has been to start from well known facts about the Wigner transforms and to keep the derivations at the simplest level consistent with obtaining all the structural formulas needed for the line shape problem. Nevertheless, we note that in the approximate theory given in Section 4, the space \mathcal{H}_1 is replaced by an N -dimensional subspace $\mathcal{H}_1^{(N)}$ and so the mixed symbols become $N \times N$ matrix functions. For matrix valued symbols the rigorous methods and convergence estimates of pseudodifferential operator analysis (cf. Appendix A) will be applicable with straightforward modifications.

A precursor of the mixed Weyl symbol formalism, employing matrix valued symbols, was used in [27] to obtain equations of motion for quantum mean values in a Schrödinger evolution problem with a Hamiltonian containing spin structure. There one also finds an analog of the classical path approach.

3. Interaction Picture Dynamics

The final form of line shape theory we devise utilizes the interaction picture generated by the perturber Hamiltonian, \widehat{H}_2 . In this description an observable \widehat{A} acquires a time dependent form $\widehat{A}(\tau) = \mathbf{\Gamma}(H_2; \tau) \widehat{A} \equiv U(\widehat{H}_2; \tau)^\dagger \widehat{A} U(\widehat{H}_2; \tau)$. The operator $\mathbf{\Gamma}(H_2; \tau)$ denotes the \widehat{H}_2 Heisenberg evolution on \mathcal{H} . When this interaction picture flow is stated in the σ_2 -mixed symbol representation, it becomes

$$\sigma_2(\mathbf{\Gamma}(H_2; \tau) \widehat{A})(z) = (\Gamma(H_2; \tau) \sigma_2 \widehat{A})(z) \equiv \widehat{A}_{w2}(\tau|z) . \quad (3.1)$$

Here $\Gamma(H_2; \tau) \equiv \sigma_2 \mathbf{\Gamma}(H_2; \tau) \sigma_2^{-1}$ denotes the fundamental evolution operator that maps the initial mixed symbol $\widehat{A}_{w2}(z)$ into its dynamical value $\widehat{A}_{w2}(\tau|z)$.

In this section, a semiclassical approximation of $\Gamma(H_2; \tau)$ based on the quantum trajectories generated by $\widehat{H}_2 = I_1 \otimes \hbar_2$ is constructed. The structure of the expansion closely parallels that found in Section I cf. (1.6) and in references [3, 28]. This prior work developed the semiclassical asymptotics for the (\mathbf{C} -valued) Weyl symbol description of quantum mechanics. However, in the present circumstance $\widehat{A}_{w2}(\tau|z)$ is an \mathcal{H}_1 -operator valued symbol. The approach introduced in reference [3] was to use quantum trajectories

as a basis from which to construct the full semiclassical expansion. The arguments below show that this idea remains applicable to the study of the mixed Weyl symbol evolution $\Gamma(H_2; \tau)$.

In Section 2, the dimensionless parameter ϵ was introduced to describe the idea of scaling \hbar to zero. We maintain this notation in this section and display this scaling as $\epsilon\hbar \rightarrow 0$. The semiclassical representations found in this section presume that the σ_2 symbols for \widehat{H}_2 and \widehat{A} admit $\epsilon\hbar \rightarrow 0$ asymptotic expansions. This is indeed the case here, where both \widehat{H}_2 and \widehat{A} have \hbar independent symbols.

3.1. Quantum Trajectories

Let the static canonical operators $\{\widehat{z}_\alpha\}_1^{2d_2}$ be restricted to the space \mathcal{H}_2 and let $\widehat{z}_\alpha(\tau) = \mathbf{\Gamma}(h_2; \tau)\widehat{z}_\alpha$ denote the associated \widehat{h}_2 Heisenberg evolution. The quantum trajectories are defined as $\mathbf{z}_\alpha(\tau|z) = \Gamma(h_2; \tau)\pi_\alpha(z) = (\widehat{z}_\alpha(\tau))_{\mathbf{w}}(z)$ and obey the equation of motion

$$\frac{\partial}{\partial \tau} \mathbf{z}_\alpha(\tau|z) = \{\mathbf{z}_\alpha(\tau), h_2\}_{\mathbf{M}}(z) . \quad (3.2a)$$

In this identity, $\{\cdot, \cdot\}_{\mathbf{M}}$ is the Moyal bracket defined for \mathbf{C} -valued Weyl symbols supported on T_2^* . At $\tau = 0$, the initial condition for \mathbf{z}_α is $\mathbf{z}_\alpha(0|z) = \pi_\alpha(z) = z_\alpha$. Equation (3.2a) is an important example of (1.5b).

An approximate solution of $\mathbf{z}_\alpha(\tau|z)$ is obtained by expanding (3.2a) in small ϵ . That this is possible is a result of the standard[2] small ϵ asymptotic expansion of the Moyal bracket, cf. (2.8)

$$\{\mathbf{z}_\alpha(\tau), h_2\}_{\mathbf{M}}(z) = \{\mathbf{z}_\alpha(\tau), h_2\}(z) + \sum_{n=1}^{\infty} \frac{(-1)^n (\epsilon\hbar/2)^{2n}}{(2n+1)!} B^{2n+1} \prec \mathbf{z}_\alpha(\tau), h_2 \succ (z) . \quad (3.2b)$$

Using (3.2b) in (3.2a) and solving for the coefficient functions order by order in ϵ , one finds[3, Sec. III]

$$\mathbf{z}_\alpha(\tau|z) = \sum_{n=0}^{\infty} \frac{(\epsilon\hbar)^n}{n!} \mathbf{z}_\alpha^{(n)}(\tau|z) = g_\alpha(\tau|z) + \frac{(\epsilon\hbar)^2}{2} \mathbf{z}_\alpha^{(2)}(\tau|z) + O(\epsilon^4) . \quad (3.2c)$$

The leading term above is the solution of Hamilton's equation

$$\dot{g}(\tau|z) = J^{(2)} \nabla h_2(g(\tau|z)) , \quad (3.2d)$$

with initial condition $g(0|z) = z$. Because both the Moyal bracket and h_2 are even functions of \hbar , one can prove that $\mathbf{z}_\alpha(\tau|z)$ (cf. [3] Lemma 5) is an \hbar -even function. As a result, all n odd terms vanish in expansion (3.2c). The higher order correction functions $\mathbf{z}_\alpha^{(n)}(\tau|z)$, $n \geq 2$, are obtained by solving an inhomogeneous Jacobi field equation, (cf. 3.9b). The classical flow $g(\tau|z)$ and coefficients $\mathbf{z}_\alpha^{(2)}(\tau|z)$ are defined and finite for all time displacements τ .

3.2. Semiclassical Asymptotics of $\Gamma(H_2; \tau)$

In this subsection, the $\epsilon\hbar \rightarrow 0$ asymptotic expansion for $\Gamma(H_2; \tau)$ is derived. To start, we note that it is useful to reorganize the Fourier integral formulas for \hat{A} and $\hat{A}_{w2}(z)$ in the following manner. Given $A_w(Z; z)$ with Fourier dual $a(U; u)$, set

$$\hat{A}(u) \equiv \int dU a(U; u) e^{iU \cdot \hat{Z}}. \quad (3.3a)$$

The quantity $\hat{A}(u)$ is a u -parameter function with \mathcal{H}_1 operator values. Representations (2.2c) and (2.3b) now read

$$\hat{A} = \int du \hat{A}(u) e^{iu \cdot \hat{z}}, \quad (3.3b)$$

$$\hat{A}_{w2}(z) = \int du \hat{A}(u) e^{iu \cdot z}. \quad (3.3c)$$

The action of $\Gamma(H_2; \tau)$ on \hat{A} has the integral form

$$\Gamma(H_2; \tau) \hat{A} = \int du \hat{A}(u) e^{iu \cdot \hat{z}(\tau)}. \quad (3.3d)$$

Note that the integrand in (3.3d) may be restated as $e^{iu \cdot \hat{z}(\tau)} = e^{(\hat{z}(\tau) - s) \cdot \nabla_z} e^{iu \cdot (s+z)}|_{z=0}$. Here s is an arbitrary vector in \mathbf{R}^{d_2} , and $\hat{z}(\tau) - s$ is shorthand for $\hat{z}(\tau) - sI_2$. Combining this with (3.3d) gives one an operator valued power series

$$\begin{aligned} \Gamma(H_2; \tau) \hat{A} &= \exp[(\hat{z}(\tau) - s) \cdot \nabla_z] \hat{A}_{w2}(s+z)|_{z=0} \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} (\hat{z}(\tau) - s)_{\mu_1} \cdots (\hat{z}(\tau) - s)_{\mu_n} \hat{A}_{w2; \mu_1 \cdots \mu_n}(s). \end{aligned} \quad (3.3e)$$

Obviously, in this formula, $\hat{A}_{w2; \mu_1 \cdots \mu_n}(s)$ is a static operator, while all the dynamics resides in the $\hat{z}(\tau) - s$ factors. Convert (3.3e) into an identity for $\Gamma(H_2; \tau)$ by the application of the transform σ_2 to obtain

$$\Gamma(H_2; \tau) \hat{A}_{w2}(z) = \sum_{n=0}^{\infty} \frac{1}{n!} (\mathbf{z}(\tau) - s)_{\mu_1} * \cdots * (\mathbf{z}(\tau) - s)_{\mu_n} \hat{A}_{w2; \mu_1 \cdots \mu_n}(s). \quad (3.4)$$

The series (3.4) is an s -dependent family of representations for the s -independent object $\Gamma(H_2; \tau) \hat{A}_{w2}(z)$. An optimal choice of s will make the n th series coefficient of order $O(\epsilon^{l(n)})$, where $l(n) \geq n/2$. For each given τ, z choose $s = \mathbf{z}(\tau|z)$. This makes the $n = 1$ term zero, and gives us the expansion

$$\Gamma(H_2; \tau) \hat{A}_{w2}(z) = \hat{A}_{w2}(\mathbf{z}(\tau|z)) + \sum_{n=2}^{\infty} \frac{1}{n!} W_{\mu_1 \cdots \mu_n}(\tau|z) \hat{A}_{w2; \mu_1 \cdots \mu_n}(\mathbf{z}(\tau|z)), \quad (3.5a)$$

$$W_{\mu_1 \cdots \mu_n}(\tau|z) = S_n(\mathbf{z}_{\mu_1}(\tau) - s_{\mu_1}) * \cdots * (\mathbf{z}_{\mu_n}(\tau) - s_{\mu_n})(z) |_{s=\mathbf{z}(\tau|z)}. \quad (3.5b)$$

Here S_n is the permutation group operator ($S_n^2 = S_n$) that averages over all the $n!$ reorderings of the indices (μ_1, \cdots, μ_n) . The $*$ products in (3.5b) must be evaluated

before the constraint $s = \mathbf{z}(\tau|z)$ is imposed. In this evaluation the quantity s is a z -independent constant. The average S_n ensures that the coefficient functions W are real and permutation invariant in the indices (μ_1, \dots, μ_n) .

An efficient way to compute the W functions is via the link operator L that expresses the extent to which the $*$ product differs from commutative multiplication. This operator is $L_{jk} \equiv \exp(\frac{i\epsilon\hbar}{2}B_{jk}) - 1$. It acts on an n -tuple of phase space functions $\prec A_1(z^{(1)}), A_2(z^{(2)}), \dots, A_n(z^{(n)}) \succ$. The labels jk specify which pair of the n -tuple elements that B acts on prior to diagonal evaluation at $z^{(1)} = \dots = z^{(n)} = z$. The link operator is $O(\epsilon)$. A short calculation gives

$$\begin{aligned} W_{\mu_1\mu_2}(\tau|z) &= L_{12}S_2 \prec \mathbf{z}_{\mu_1}(\tau), \mathbf{z}_{\mu_2}(\tau) \succ (z) \\ &= \frac{1}{8}(\epsilon\hbar)^2 B_{12}^2 S_2 \prec \mathbf{z}_{\mu_1}(\tau), \mathbf{z}_{\mu_2}(\tau) \succ (z) + O(\epsilon^4), \end{aligned} \quad (3.6a)$$

$$\begin{aligned} W_{\mu_1\mu_2\mu_3}(\tau|z) &= (L_{12}L_{13}L_{23} - L_{12}L_{23})S_3 \prec \mathbf{z}_{\mu_1}(\tau), \mathbf{z}_{\mu_2}(\tau), \mathbf{z}_{\mu_3}(\tau) \succ (z) \\ &= \frac{1}{4}(\epsilon\hbar)^2 B_{12}B_{23}S_3 \prec \mathbf{z}_{\mu_1}(\tau), \mathbf{z}_{\mu_2}(\tau), \mathbf{z}_{\mu_3}(\tau) \succ (z) + O(\epsilon^4). \end{aligned} \quad (3.6b)$$

A couple of remarks about representation (3.5)–(3.6) are in order. If $\hat{A}_{w2}(z)$ is a polynomial in z , then the series (3.5a) truncates at finite order and provides exact expressions for $\Gamma(H_2; \tau)\hat{A}_{w2}(z)$. In essence expansion (3.5) is a semiclassical expansion for an arbitrary mixed symbol \hat{A}_{w2} . It employs $\mathbf{z}(\tau|z)$ (quantum flow) transport with higher order corrections arising from $W_{\mu_1\dots\mu_n}(\tau|z)$. The link operator L was introduced in reference [3] in order to determine the symbol of an exponential operator $\exp \hat{A}$ in terms of A_w .

3.3. The Standard Approximation

Although expansion (3.5) is the basic semiclassical expansion for $\Gamma(H_2; \tau)$, it is nevertheless not convenient for numerical calculation. If H_2 is z quadratic then $\mathbf{z}(\tau|z) = g(\tau|z)$ and $W_{\mu_1\dots\mu_n}(\tau|z) = 0$. In this case the first term is exact, i.e. $\Gamma(H_2; \tau)\hat{A}_{w2}(z) = \hat{A}_{w2}(g(\tau|z))$. Generally, for $n > 0$, $\mathbf{z}^{(n)}(\tau|z)$ and $W_{\mu_1\dots\mu_n}(\tau|z)$ do not vanish and for increasing n these functions are difficult to numerically compute.

In order to build a more computationally accessible approximation one combines expansion (3.2c) for $\mathbf{z}(\tau|z)$ with (3.5) and collects all terms of common ϵ order. This results in an expansion of the form

$$\Gamma(H_2; \tau)\hat{A}_{w2}(z) = \sum_{n=0}^{\infty} \frac{(\epsilon\hbar)^{2n}}{(2n)!} \gamma^{(2n)}(H_2; \tau)\hat{A}_{w2}(z). \quad (3.7a)$$

The coefficient operators $\gamma^{(n)}(H_2; \tau)$ are composed of transport along $g(\tau|z)$ plus a z -derivative structure inherited from (3.5a). The first term is pure classical transport

$$\gamma^{(0)}(H_2; \tau)\hat{A}_{w2}(z) = \hat{A}_{w2}(g(\tau|z)), \quad (3.7b)$$

while the $O(\epsilon^2)$ term reads

$$\begin{aligned} \gamma^{(2)}(H_2; \tau) \hat{A}_{w2}(z) &= \mathbf{z}_\mu^{(2)}(\tau|z) \hat{A}_{w2;\mu}(g(\tau|z)) - \frac{1}{8} w_{\mu\nu}(\tau|z) \hat{A}_{w2;\mu\nu}(g(\tau|z)) \\ &\quad + \frac{1}{12} w_{\mu\nu\lambda}(\tau|z) \hat{A}_{w2;\mu\nu\lambda}(g(\tau|z)) . \end{aligned} \quad (3.7c)$$

The lower case w coefficients result from the suitably scaled limits of the functions W . Since $W = O(\epsilon^2)$ for W 's with two and three indices, one has

$$w_{\mu\nu}(\tau|z) = \lim_{\epsilon \rightarrow 0} (\epsilon \hbar)^{-2} W_{\mu\nu}(\tau|z) = B_{12}^2 \prec g_\mu(\tau), g_\nu(\tau) \succ (z) , \quad (3.8a)$$

$$\begin{aligned} w_{\mu\nu\lambda}(\tau|z) &= \lim_{\epsilon \rightarrow 0} (\epsilon \hbar)^{-2} W_{\mu\nu\lambda}(\tau|z) = B_{12} B_{23} \prec g_\mu(\tau), g_\nu(\tau), g_\lambda(\tau) \succ (z) \\ &= -J^{(2)} \nabla g_\mu(\tau|z) \cdot \nabla \nabla g_\nu(\tau|z) \cdot J^{(2)} \nabla g_\lambda(\tau|z) . \end{aligned} \quad (3.8b)$$

These formulas make it evident that the w coefficients are functions of the classical flow $g(\tau|z)$.

A common building block in the expressions for $\gamma^{(n)}(H_2; \tau)$ is the Jacobi field $\nabla g(\tau|z)$ and its higher order derivatives $\nabla \nabla g(\tau|z)$, etc. Jacobi fields describe the stability of a trajectory $g(\tau|z)$ with respect to small changes of its initial data. Differentiating (3.2d) in the parameter z yields

$$\mathcal{J}(\tau) \nabla g(\tau|z) \equiv \left[\frac{d}{d\tau} - J^{(2)} \nabla \nabla h_2(g(\tau|z)) \right] \nabla g(\tau|z) = 0 . \quad (3.9a)$$

The solutions of (3.9a) with zero right-hand side are called Jacobi fields. The initial condition is $\nabla g(0|z) = \delta$ (the $2d_2$ identity matrix). Related functions $\nabla \nabla g(\tau|z)$ solve a modified form of (3.9a) with a non-zero inhomogenous term [28, Eq. (3.11)]. Finally, $\mathbf{z}^{(2)}(\tau|z)$ is the solution of the $2d_2$ system of ODE's

$$\begin{aligned} \mathcal{J}(\tau)_{\mu\nu} \mathbf{z}_\nu^{(2)}(\tau|z) &= -\frac{1}{8} w_{\mu_1\mu_2}(\tau|z) J_{\mu\lambda}^{(2)} h_{2;\mu_1\mu_2\lambda}(g(\tau|z)) \\ &\quad + \frac{1}{12} w_{\mu_1\mu_2\mu_3}(\tau|z) J_{\mu\lambda}^{(2)} h_{2;\mu_1\mu_2\mu_3\lambda}(g(\tau|z)) , \end{aligned} \quad (3.9b)$$

with initial conditions $\mathbf{z}_\mu^{(2)}(0|z) = 0$.

We refer to expansion (3.7) as the *standard semiclassical expansion* of $\Gamma(H_2; \tau)$. The basic structure of $\gamma^{(n)}(H_2; \tau)$ is consistent with that derived in reference [3]. The new feature here is that the target object \hat{A}_{w2} is operator valued. In the case where the target symbol is \mathbf{C} -valued, the existence of small ϵ expansions of the standard form have been known for a considerable time. These alternate approaches [15, 16, 3, 17] are based on restructuring the Moyal equation of motion into a classical inhomogeneous Poisson bracket equation of motion. The inhomogenous component is formed from the non-leading terms of the derivative expansion of the bracket $\{\cdot, \cdot\}_M$. Again one finds the leading $O(\epsilon^0)$ term is classical transport. However, the higher order $O(\epsilon^n), n \geq 2$,

terms have representations [3, Eq.(4.16)] that are substantially more complicated than the $\gamma^{(2)}(H_2; \tau)$ formula (3.7c).

Recently an extensive numerical study [28] of the effectiveness of the two term asymptotic expansion (1.6b) was carried out. For systems with identical atom–atom pairs, such as helium, neon and argon, the time evolution of quantum expectation values was computed. The pair interaction in these systems was a phenomenologically determined Lennard–Jones potential. There was no difficulty in computing the functions $(g_\mu(\tau|z), \mathbf{z}_\mu^{(2)}(\tau|z), w_{\mu\nu}(\tau|z)$ and $w_{\mu\nu\lambda}(\tau|z))$ which enabled the construction of $\gamma^{(0)}(h_2; \tau)$ and $\gamma^{(2)}(h_2; \tau)$. The scattering problem was investigated for a variety of Gaussian initial states and observables. In most instances the $\gamma^{(0)}(h_2; \tau)$ term dominated the contributions of $\gamma^{(2)}(h_2; \tau)$ to the expectation value.

One factor favoring the good convergence of expansion (1.6b), in the problems of interest here, is that the classical system is completely integrable. This means that the classical flow is not chaotic. In particular, this implies that for almost all $z \in T_2^*$ the Jacobi field $\nabla g(\tau|z)$ can not have exponential growth in τ . Nevertheless, there exists a set of unstable classical trajectories in this problem. All these motions are associated with an unstable equilibrium point. These points occur when the radial potential energy $v_e(r) \equiv v(r) + L^2/(2mr^2)$ (for a given angular momentum L) has $v_e'(r) = 0$, with $v_e''(r) < 0$. Associated with this fixed point one obtains unstable orbits with positive Lyapunov exponent. The numerical studies we completed establish that the $n = 2$ term expansion (1.6b) is inaccurate for large time displacements in the small region of phase space surrounding the unstable fixed points. In this neighborhood of phase space, one must devise a different approximation for $\Gamma(h_2; \tau)$. Several alternatives for overcoming this difficulty are offered in Section 5.

4. Autocorrelation Representations

The evolution $\Gamma(H; t)\hat{\mu}_j = U(H; t)^\dagger \hat{\mu}_j U(H; t)$ controls the time behavior of the autocorrelation function, $C(t)$. This section combines the mixed Weyl symbol formalism and the $\Gamma(H_2; t)$ semiclassical expansion of Section 3 to construct numerically accessible approximate representations of $C(t)$.

First it is helpful to reformulate $C(t)$, cf. (1.3), in terms of the H_2 picture evolution. Let $\tilde{U}(t) \equiv U(H; t)U(H_2; t)^\dagger$; within the \widehat{H}_2 interaction picture framework, $\tilde{U}(t)$ determines the full \widehat{H} dynamics. From the Schrödinger evolution equations for $U(H; t)$ and $U(H_2; t)$, it follows that $\tilde{U}(t)$ is generated by the time dependent Hamiltonian,

$$\tilde{H}(t) \equiv \Gamma(H_2; -t)(\widehat{H}_1 + \widehat{H}_{12}) = \widehat{H}_1 + \Gamma(H_2; -t)\widehat{H}_{12}, \quad (4.1a)$$

$$i\hbar \frac{\partial}{\partial t} \tilde{U}(t) = \tilde{U}(t)\tilde{H}(t). \quad (4.1b)$$

The operator $\tilde{U}(t)$ is unitary and has initial condition $\tilde{U}(0) = I$. The appearance of

$\widetilde{H}(t)$ to the right of $\widetilde{U}(t)$ is characteristic of a backward evolution equation.

Conjugation of \hat{A} by $\widetilde{U}(t)$ defines a Heisenberg evolution $\widetilde{\Gamma}(t)$ on \mathcal{H} in the standard way, $\widetilde{\Gamma}(t)\hat{A} \equiv \widetilde{U}(t)^\dagger \hat{A} \widetilde{U}(t)$. Knowledge of the evolutions $\widetilde{\Gamma}(t)$ and $\Gamma(H_2; -t)$ provides an alternate way of determining the correlation function. Employing the cyclic invariance of the trace and the commutation relation $[\hat{\mu}_j, \widehat{H}_2] = 0$ allows one to represent (1.3) as

$$C(t) = \text{Tr}_{\mathcal{H}} \left[\left(\widetilde{\Gamma}(t) \hat{\mu}_j \right) \left(\Gamma(H_2; -t) \hat{\rho} \right) \hat{\mu}_j \right]. \quad (4.2)$$

Whenever $[\hat{\rho}, \widehat{H}_2] = 0$, the density matrix is time independent, i.e. $\Gamma(H_2; -t)\hat{\rho} = \hat{\rho}$. In most applications, the anisotropic interaction \widehat{H}_{12} is small relative to \widehat{H}_1 and \widehat{H}_2 . This means that the radiator and perturber systems are weakly coupled and that the density matrix is accurately approximated by the tensor product of the form, $\hat{\rho}_1(h_1) \otimes \hat{\rho}_2(h_2)$. For a system with radiators initially in the ground state, we may take the effective density matrix to be $\hat{\rho} = |\Phi_1\rangle\langle\Phi_1| \otimes e^{-\beta\widehat{h}_2}$. We use this latter form of the density matrix throughout Section 4.

4.1. Exact Mixed Symbol Dynamics

The trace identity (2.13b) determines $C(t)$ in terms of the T_2^* phase space integral of $(\widetilde{\Gamma}(t)\hat{\mu}_j)_{\text{w}2}(z)$ and $(\hat{\rho}\hat{\mu}_j)_{\text{w}2}(z) = (e^{-\beta\widehat{h}_2})_{\text{w}}(z)|\Phi_1\rangle\langle\Phi_1|\hat{\mu}_j$. At this stage one needs an equation of motion for $\widetilde{\Gamma}(t)$ dynamics which is stated in terms of a mixed symbol evolution operator: $(\widetilde{\Gamma}(t)\hat{A})_{\text{w}2}(z) = \widetilde{I}(t)\hat{A}_{\text{w}2}(z)$, where $\widetilde{I}(t) \equiv \sigma_2 \widetilde{\Gamma}(t) \sigma_2^{-1}$. The symbol valued Heisenberg flow $\widetilde{I}(t)\hat{A}_{\text{w}2}$ obeys

$$\frac{\partial}{\partial t} \widetilde{I}(t)\hat{A}_{\text{w}2} = \{ \widetilde{I}(t)\hat{A}_{\text{w}2}, \widetilde{H}(t)_{\text{w}2} \}_{\text{M}} \quad (4.3a)$$

with Moyal bracket (2.7c). In the present application, $\hat{A}_{\text{w}2}$ is the dipole operator $\hat{\mu}_j$. The Hamiltonian here is the mixed symbol image of (4.1a),

$$\widetilde{H}(t)_{\text{w}2}(z) = \widehat{H}_1 + \Gamma(H_2; -t)(\widehat{H}_{12})_{\text{w}2}(z). \quad (4.3b)$$

The matrix element version of (4.3a) with respect to the basis $\{|\Phi_k\rangle\}_{k=1}^\infty$ reads

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} X_{kr}^j(t|z) &= \sum_{s=1}^{\infty} \left(X_{ks}^j(t|z) * \langle \Phi_s | \widetilde{H}(t)_{\text{w}2}(z) | \Phi_r \rangle \right. \\ &\quad \left. - \langle \Phi_k | \widetilde{H}(t)_{\text{w}2}(z) | \Phi_s \rangle * X_{sr}^j(t|z) \right). \end{aligned} \quad (4.3c)$$

where $X_{kr}^j(t|z) \equiv \langle \Phi_k | (\widetilde{I}(t)\hat{\mu}_j)(z) | \Phi_r \rangle$. This latter definition implies the z -independent initial condition $X_{kr}^j(0|z) \equiv \langle \Phi_k | \hat{\mu}_j | \Phi_r \rangle$.

Given the solution of (4.3c), the correlation function is represented as

$$\begin{aligned} C(t) &= \frac{1}{h^3} \int_{T_2^*} dz \text{Tr}_{\mathcal{H}_1} (\widetilde{I}(t)\hat{\mu}_j)(z) * (\hat{\rho}\hat{\mu}_j)_{\text{w}2}(z) \\ &= \frac{1}{h^3} \sum_{k=1}^{\infty} \int_{T_2^*} dz X_{k1}^j(t|z) X_{1k}^j(0|z) (e^{-\beta\widehat{h}_2})_{\text{w}}(z). \end{aligned} \quad (4.4)$$

The second version of (4.4) uses the complete basis $\{|\Phi_k\rangle\}_{k=1}^\infty$ to evaluate the \mathcal{H}_1 trace. Since the integrand is just the product of two symbols, cf. (2.14), the $*$ operation may be removed. Throughout this section the dimension $d_2 = 3$.

4.2. Approximate Mixed Symbol Dynamics

For typical molecular systems, equations (4.3c) are too difficult to solve exactly. Further progress depends on developing approximate solutions that take advantage of the type of physics present in the line shape problem and the opportunities for simplification inherent in the mixed symbol formalism. The statement of exact dynamics provides a point of departure for the construction of various approximating methods. Possible options are the conversion of (4.3c) into an integral equation, the use of perturbation theory, and the development of an eikonal representation. The approach we take here is to focus on the semiclassical structure. The subsequent reductions of (4.3) rest on three approximations:

1) It is assumed that only a small number of \widehat{h}_1 eigenstates $\{|\Phi_k\rangle\}_{k=1}^N$ significantly couple to each other. This means that \mathcal{H}_1 is replaced by the finite dimensional vector space, $\mathcal{H}_1^{(N)}$, spanned by the basis $\{|\Phi_k\rangle\}_{k=1}^N$.

2) The Hamiltonian, $\widetilde{H}(t)_{w2}(z)$, may be approximated by the standard semiclassical expansion of Section 3, namely,

$$\begin{aligned}\widetilde{H}(t)_{w2}(z) &= \widehat{H}_1 + \sum_{n=0}^{\infty} \frac{(\epsilon\hbar)^{2n}}{(2n)!} \gamma^{(2n)}(H_2; -t)(\widehat{H}_{12})_{w2}(z). \\ &= \widehat{H}_1 + (\widehat{H}_{12})_{w2}(g(-t|z)) + \frac{(\epsilon\hbar)^2}{2!} \gamma^{(2)}(H_2; -t)(\widehat{H}_{12})_{w2}(z) + O(\epsilon^4).\end{aligned}\quad (4.5)$$

3) The Moyal bracket on the right of (4.3a) can be replaced with leading terms of the small ϵ expansion (2.11b).

Solvable reduced equations of motion are realized by applying approximations 1)–3). The finite coupled state assumption 1) is applicable when the range of thermal energies available in the collision process can excite a limited set of radiator eigenstates. The next stage is to employ the semiclassical expansion 2) valid to order $O(\epsilon^2)$. In this approximation, the H_{12} part of $\widetilde{H}_{w2}(t)$ defines an $O(\epsilon^1)$ consistent time and state dependent molecular interaction by $M_{kr}(t|z) \equiv \langle \Phi_k | (\widehat{H}_{12})_{w2}(g(-t|z)) | \Phi_r \rangle$. The modified version of (4.3c) thus becomes the $N \times N$ system

$$\begin{aligned}i\hbar \frac{\partial}{\partial t} \chi_{kr}^j(t|z) &= (E_r - E_k) \chi_{kr}^j(t|z) \\ &+ \sum_{s=1}^N \left[\left(\chi_{ks}^j(t|z) * M_{sr}(t|z) - M_{ks}(t|z) * \chi_{sr}^j(t|z) \right) \right].\end{aligned}\quad (4.6)$$

The initial condition for (4.6) is $\chi_{kr}^j(0|z) = \langle \Phi_k | \widehat{\mu}_j | \Phi_r \rangle$. The $(E_r - E_k) \chi_{kr}^j(t|z)$

contribution arises from the \widehat{H}_1 part of $\widetilde{H}(t)_{w2}(z)$. The notation $\chi^j(t|z)$ is used to distinguish the approximate solutions of (4.6) from the exact $X^j(t|z)$.

Observe that the non-zero term $(E_r - E_k)\chi_{kr}^j(t|z)$ in (4.6) means that the $i\hbar$ factor in front of the time derivative term can not cancel against a similar \hbar multiplier on the right-hand side. In this sense (4.6) is very different in its \hbar analytic structure than the Moyal equation of motion (1.5b), where such cancellation does occur. This means that methods for approximately solving (4.6) are not close parallels of the standard semiclassical expansions, (1.6b) or (3.7a).

The zeroth order reduction of (4.6) results if one replaces the $*$ operation by ordinary multiplication to obtain the matrix ODE system

$$i\hbar \frac{\partial}{\partial t} \chi_{kr}^{0,j}(t|z) = (E_r - E_k) \chi_{kr}^{0,j}(t|z) + \sum_{s=1}^N \left[\left(\chi_{ks}^{0,j}(t|z) M_{sr}(t|z) - M_{ks}(t|z) \chi_{sr}^{0,j}(t|z) \right) \right]. \quad (4.7)$$

At this level of truncation one has recovered the classical path approximations to the line shape theory. The associated correlation function results from replacing $X^j(t|z)$ in (4.4) with $\chi^{0,j}(t|z)$ and restricting the k sum to N terms. To further clarify this point consider again the rigid rotor example, cf. (1.2b). Write the classical flow generated by h_2 in terms of its coordinate and momentum parts: $g(t|z) = (q(t|z), p(t|z))$. The molecular interaction M becomes

$$M_{kr}(t|z) = \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} V_{12}^{(l)}(|q(-t|z)|) \sum_{m=-l}^{m=l} Y_{lm}^*(\widehat{q}(-t|z)) \langle \Phi_k | Y_{lm}(\widehat{Q}) | \Phi_r \rangle. \quad (4.8)$$

As is evident, the anisotropic interaction potential $V_{12}^{(l)}$ is evaluated along the classical path $q(-t|z)$. The states $\{|\Phi_k\rangle\}$ are eigenstates of the \mathcal{H}_1 system angular momenta, J^2 and J_z . This means that $\langle \Phi_k | Y_{lm}(\widehat{Q}) | \Phi_r \rangle$ has an explicit evaluation in terms of Clebsch-Gordan coefficients. Viewed as a phase space function $M(t|z)$ is a time dependent $\mathcal{H}_1^{(N)}$ valued symbol which is ϵ independent.

Now consider solutions of (4.6) that include the leading noncommutative $*$ effects. We organize this family of approximations as an asymptotic series in the small parameter ϵ , which describes the deformation of the σ_2 -star product, cf. (2.10b), about conventional \mathcal{H}_1 operator multiplication,

$$\chi_{kr}^j(t|z) = \sum_{n=0}^{\infty} \epsilon^n \chi_{kr}^{n,j}(t|z) = \chi_{kr}^{0,j}(t|z) + \epsilon \chi_{kr}^{1,j}(t|z) + O(\epsilon^2). \quad (4.9a)$$

The leading term $\chi_{kr}^{0,j}(t|z)$ is the classical path approximation. Placing (4.9a) in (4.6) and extracting the equation for $\chi^{1,j}(t|z)$ gives

$$i\hbar \frac{\partial}{\partial t} \chi_{kr}^{1,j}(t|z) = (E_r - E_k) \chi_{kr}^{1,j}(t|z) + \sum_{s=1}^N \left[\left(\chi_{ks}^{1,j}(t|z) M_{sr}(t|z) - M_{ks}(t|z) \chi_{sr}^{1,j}(t|z) \right) \right]$$

$$+\frac{i\hbar}{2}J_{\alpha\beta}^{(2)}\left(\frac{\partial}{\partial z_{\alpha}}\chi_{ks}^{0,j}(t|z)\frac{\partial}{\partial z_{\beta}}M_{sr}(t|z)-\frac{\partial}{\partial z_{\alpha}}M_{ks}(t|z)\frac{\partial}{\partial z_{\beta}}\chi_{sr}^{0,j}(t|z)\right)\Big]. \quad (4.9b)$$

Here the initial condition is $\chi_{kr}^{1,j}(0|z) = 0$. The form of this equation for $\chi^{1,j}$ is a version of (4.7) with an inhomogeneous term added. The $J_{\alpha\beta}^{(2)}$ term on the right of (4.9b) records, to leading order, the noncommutative nature of the $*$ product. The z derivatives of the interaction M may be expressed via the Jacobi fields of the classical trajectories. By the chain rule one has

$$\frac{\partial}{\partial z_{\alpha}}M_{sr}(t|z) = \langle \Phi_s | [\nabla_{\gamma}(\widehat{H}_{12})_{w2}] (g(-t|z)) | \Phi_r \rangle g_{\gamma;\alpha}(-t|z). \quad (4.9c)$$

The pattern one sees in (4.9b) for the determination of $\chi_{sr}^{0,j}$ and $\chi_{sr}^{1,j}$ continues to higher order. Given the values of $\{\chi_{kr}^{l,j}\}_{l=0}^{n-1}$ the ODE system for $\chi_{kr}^{n,j}$ results from combining (4.6), (4.9a) with the $*$ expansion (2.10). Normally, one would employ expansions 2) and 3) to a common order. Thus the $O(\epsilon^2)$ consistent calculation of $\chi_{kr}^{2,j}$ requires the addition of the $\gamma^{(2)}(H_2; -t) \langle \Phi_k | (\widehat{H}_{12})_{w2}(z) | \Phi_r \rangle$ contribution to $M_{kr}(t|z)$.

Evaluation of the integral (4.4) is demanding because $\chi_{kr}^j(t|z)$ needs to be numerically determined for each point z in the six dimensional phase space T_2^* . However the number of integration variables may be significantly reduced by using the spherical tensor structure present in this problem. The quantities $(\tilde{\Gamma}(t)\hat{\mu}_j)_{w2}(z)$ and $(e^{-\beta\hat{h}_2})_w(z)\hat{\mu}_j$ are rank one tensors whose contraction is a scalar. One may reduce integration (4.4) to three parameters by representing $z = (q, p)$ by the three Euler angles and three rotational invariants $|q|, |p|$ and $q \cdot p$. The Euler angle integrals involve Wigner functions $\mathcal{D}_{M,M'}^J(\alpha, \beta, \gamma)$ and can be done analytically. As an example of this type of phase space tensor reduction, see [28, Section III].

The method of approximating $X_{kr}^j(t|z)$ by the system of equations (4.9) depends upon representing the σ_2 -star product by its leading ϵ terms. In the computation of observables one must have $\epsilon = 1$. As discussed in Appendix A this is an asymptotic derivative expansion. Roughly speaking, it will succeed if the higher order terms $B^n \prec X_{kr}^j(t), M_{sr}(t) \succ (z)$, $n \geq 2$ are small.

It is useful to consolidate the correlation function results into a single statement. Assuming that $\chi_{kr}^{0,j}$ and $\chi_{kr}^{1,j}$ are solutions of (4.7) and (4.9b), respectively, the $O(\epsilon^1)$ representation is

$$C(t) = \frac{1}{\hbar^3} \sum_{k=1}^N \langle \Phi_1 | \hat{\mu}_j | \Phi_k \rangle \int_{T_2^*} dz \left(\chi_{k1}^{0,j}(t|z) + \chi_{k1}^{1,j}(t|z) \right) (e^{-\beta\hat{h}_2})_w(z). \quad (4.10)$$

In our view the appropriate test of success of the approximating methods introduced here will be through numerical implementation and application to specific molecular systems.

The correlation function formulas (4.4) and (4.10) assume that the perturber could be treated as a point particle. This restriction is easy to relax, by enlarging the

Hilbert space \mathcal{H}_1 to include both the radiator and perturber internal degrees of freedom. Likewise, the presumed $t = 0$ state of the system $\hat{\rho} = |\Phi_1\rangle\langle\Phi_1| \otimes e^{-\beta\hat{h}_2}$ can take a variety of alternate forms which allow a superposition of molecular eigenstates $\{|\Phi_j\rangle\}_1^N$ and the replacement of $e^{-\beta\hat{h}_2}$ by any function of \hat{h}_2 . The correlation function of interest here is based on the dipole operator $\hat{\mu}_j$. However, the method of this section continues to apply if $\hat{\mu}_j$ is replaced by any operator \hat{A} having a \hbar -regular[24, 25, 16] mixed symbol.

5. Conclusions

The spectral profile of the intensity of an emission or absorption line is the Fourier transform of the dipole autocorrelation function $C_N(t)$. In this paper we have introduced a mixed Weyl symbol formalism to represent the dynamics needed to construct the single perturber $C(t)$. Within this approach, the radiator–perturber relative separation variables are characterized by the phase space T_2^* , which serves as the support for the operator valued mixed symbols. Expectation values and in particular $C(t)$ are realized, cf. (4.4), by a phase space average over traces of the product of symbols. The result is a fully quantum theory of spectral line shapes. In the mixed symbol representation there is never any need to refer to perturber wave packets.

Furthermore, the symbol equation of motion (4.6) for the time evolving dipole moment, $\chi_{kr}^j(t|z)$, admits a natural semiclassical expansion which is based on the derivative expansion of the Moyal bracket. The mixed symbol formalism embeds within itself the classical path approximation, which appears as the leading order of the semiclassical truncation. The subsequent corrections arise from the noncommutative nature of the $*$ product for the mixed symbol.

The simplifications that result from the finite state coupling approximation 1) and the semiclassical expansions 2) and 3), give equations of motion that are suitable for numerical solution. To order $O(\epsilon^1)$ the equations (4.7) and (4.9) are no more elaborate than those previously used to numerically compute the atom–atom collision problem within the Moyal formalism, cf. [28]. The first term of (4.10) is entirely equivalent to the dipole autocorrelation function written in the classical path approximation and thus contains the same information as, for example, equation (4.2) in Griem’s treatise [29]. It must be emphasized, however, that (4.10) gives the first two terms of a completely quantum mechanical expression for $C(t)$. The established success of the classical path approximation in accounting for observed line shapes means that the $O(\epsilon^0)$ version of the theory has much of the correct physics built into it.

For heavy perturbers the classical path approximation works well. The diatomic molecular radiator–atomic perturber case has received much attention; for example, HCl–Ar collisions were studied by Nielsen and Gordon [30]. More recently, Looney and Herman [31] made a comparison of comprehensive calculations of the N_2 –broadened

rotational lines in the fundamental band of HCl with state-of-the-art experimental data [32] and found excellent agreement. Evidence that the $O(\epsilon^1)$ correction may be sufficient in many cases for an accurate quantum mechanical treatment comes from the work of Smith, Giraud and Cooper [33] on CO–He. Their classical path calculations for this light perturber system agreed with close-coupling calculations to within 10%.

Transforming the general autocorrelation function in (4.10) through (1.1) to give the profile $I(\omega)$ can be difficult. The line shape problem has two frequently employed limits, the impact approximation which applies to line centers and the quasi-static approximation which describes the far spectral wings [6]. Various unified theories have been devised to connect these two regimes. Similar strategies will have to be applied to (4.10) and (1.1) in order to compute actual profiles accurately.

The mixed symbol method of computing $C(t)$ has an important flexibility. The total isotropic intermolecular interaction energy is $v_2 + V_{12}^{(0)}$, i.e. the central potential can be arbitrarily divided between v_2 and $V_{12}^{(0)}$. It is customary, in the classical path approximation, to set $V_{12}^{(0)} = 0$. This means that the trajectories generated by $h_2 = h_{2,0} + v_2$ are consistent with the full central potential. However, one can make other choices. If $v_2 = 0$, then $h_2 = h_{2,0}$ (kinetic energy) and the classical trajectories are constant velocity straight lines. Here all the isotropic potential resides in $V_{12}^{(0)}$. For $h_{2,0}$ evolution, the $O(\epsilon^0)$ formula (4.5) in 2) is exact, namely $\widetilde{H}(t)_{w2}(z) = \widehat{H}_1 + (\widehat{H}_{12})_{w2}(g(-t|z))$. In this circumstance all the semiclassical behavior comes from approximation 3). This approach would improve upon the usual straight line trajectory technique often used to treat the broadening of atomic lines by ionic perturbers [29]. Another appealing option is to place all the attractive part of the intermolecular interaction in $V_{12}^{(0)}$. Now v_2 will be purely repulsive and for this reason the h_2 flow will not have any unstable fixed points. In this way the unstable fixed point long time breakdown [28, 34, 17] of the standard semiclassical approximation is avoided.

We have introduced the mixed Weyl symbol formalism in order to obtain a new and computationally viable full quantum version of line shape theory. However the mixed symbol representation is also applicable to any composite system having distinct quantum and semiclassical degrees of freedom. The scattering of spin dependent particles and the Coulomb excitation of an atom or a nucleus are additional examples of such systems.

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Appendix A. Derivative Expansions

The theory of pseudodifferential operators [35, 25] provides an analysis of the $*$ product and its associated derivative expansions. For \mathbf{C} -valued symbols f, g on T_2^* the $*$ product is defined by the scalar analog of (2.7b), namely

$$f * g = (\pi\hbar)^{-2d_2} \int \int dz' dz'' f(z + z') g(z + z'') \exp[2i(z' \cdot J^{(2)} z'')/\hbar]. \quad (\text{A.1})$$

In the rigorous approach there are two important questions: a) The convergence of the integral (A.1) and the status of the Groenewold series (2.8) as an asymptotic expansion of $f * g$; b) The properties of the operator corresponding to a given symbol, in particular the symbol which is the result of the $*$ product and its approximations.

The answer to these questions is effected by restricting the symbols to special classes of functions. A standard and important example is the class S^m . Take (x, ξ) to be dimensionless versions of (q, p) , and denote by S^m a set of $C^\infty(\mathbf{R}^{d_2} \times \mathbf{R}^{d_2})$ functions with estimate

$$|\nabla_x^j \nabla_\xi^k f(x, \xi)| \leq C_{jk} \langle \xi \rangle^{m-|j|}, \quad \langle \xi \rangle = \sqrt{1 + |\xi|^2} \quad (\text{A.2})$$

valid for all multi-indices $j = (j_1, \dots, j_{d_2})$, $k = (k_1, \dots, k_{d_2})$ and some constant C_{jk} , uniformly for $x \in \mathbf{R}^{d_2}$.

Then the following statements [2, Theorem (2.49)] hold: 1) The map $(f, g) \rightarrow f * g$ is continuous from $S^{m_1} \times S^{m_2} \rightarrow S^{m_1+m_2}$. 2) For $f \in S^{m_1}$ and $g \in S^{m_2}$, the remainder R_N in the Groenewold series belongs to the class $S^{m_1+m_2-N}$ and so the expansion (2.8a) becomes asymptotic. In other words, $R_N = O(\langle \xi \rangle^{m_1+m_2-N})$ and the error term vanishes as either $N \rightarrow \infty$ while $\langle \xi \rangle > 1$, or as $\langle \xi \rangle \rightarrow \infty$ while $N > m_1 + m_2$. In this sense the derivative series (2.8a) is a valid asymptotic expansion even when the small scale parameter ϵ is fixed at unity.

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